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13. ABSTRACT *(Maximum 200 words)*

By extending our previous investigations of the ternary thin-film barriers of Ta-Si-N to Mo-Si-N and W-Si-N, we have confirmed that the reason for the success of these thin-film barrier layers between Si and Cu rests on two basic features:

(i) their thermodynamic stability with Cu, and (ii) their amorphous (or near-amorphous) structure. The dependence of the electrical resistivity of these layers on the nitrogen composition further proves that at the atomic level, local order exists that concurs with that of the equilibrium phases. Structural investigations including

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small-angle x-ray scattering and high resolution transmission electron diffraction have established beyond doubt that the alloys, as they are formed by our reactive spattering process, are amorphous over large ranges of composition.

Differences between the stability of various transition metal (Tm)-Si-N alloys can be attributed to the variation of the strength with which nitrogen is bonded in the alloy. The barriers have been successfully applied to enhance the stability of n^+p shallow silicon junction diodes with a Cu metallization, as to suppress the diffusion of Cu into SiO_2.

A very complete investigation of Ti-Si-N has been initiated because this alloy has the best chance of being accepted by the industry, TiN being already an industry standard for thin-film diffusion barrier applications.

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Final Report

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Stable Contacts to Semiconductors

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The ARO grant that preceded the present one (ARO Grant DAAL03-89-K-0049, March 89- March 92) had lead to the discovery of amorphous thin-film ternary alloys of the type Ta Si N. The truly outstanding performance off these films as diffusion barriers in contact metallization of silicon devices was attributed to two particularities of these films (i) their inertrers, and (ii) their amorphous structure. The final report stated: "To prove or refute these ideas is the next major problem on the conceptual side o the subject. On the applications-oriented side, the next task is to develop a data base on the performance of other amorphous metallic alloys of this class off thin films." These two goals were those pursued in this second three-year grant.

In essence, the concept that inters and amorphouses combined are at the root o the success of these alloys has been confirmed. A major step in this direction was made by showing convincingly by model calculations that Ta Si N is a thermodynamically stable compound in contact with Ca, as the experiments in fact suggest. The prediction is generalizable: barring the possible (unknown) existence of ternary phases, all alloys of the type Tm Si N are thermodynamically stable with Cu, where Tm is a metal of the Ti, V, or Cr group (group IV B to VI B), providing Tm to Si ratio is larger than to 5:3.

Films were systematically investigated experimentally for Tm = Mo, Ta, and W and fully confirmed the prediction. It is now firmly established that these alloys form a group that include (at least) the nine elements of the transition metal groups IV B to VI B. Structural investigations including small-angle x-ray scattering and high resolution transmission electron diffraction have established beyond doubt that the alloys, as they are formed by our reactive sputtering process, are amorphous veer large ranges of composition. The simple picture of an intimate mixture of the atomic level of a metallically bonded transition metal nitride with the cavolently handed unsulating silicon nitride seems to be justified.

The fact that the nitrides have simple unit cells with of high symmetry and Si_3N_4 doesn't is another. A macroscopic expression of this is seen in the electrical resistivity o these alloys as the nitrogen content increases; there is a sudden change in the slope of the resistivity as the concentration crosses a tie-live in the constituting equilibrium compounds can only be understood if, at the atomic level, local order exists that concurs with that o the equilibrium phases.

We have made slow progress in proving experimentally that the diffusivity of Cu (or other species) in these amorphous alloys is indeed low. That in itself is a strong hint that a diffusivity is low, because atomic motions them becomes quite small. We have established an order of magnitude value of 10^{-20} Cm^2/s at 500°C for Cu in $Ta_{36}Si_{14}N_{50}$, with an activation energy of about

2.7 eV. This is of the same magnitude as Ni in SiO_2 or Si_3N_4.

The group of ternary amorphous metallic alloys includes other members than the nine Tm Si N cases cited so far. We have formed WBN films that are as good diffusion barriers for Cu as most Tm SI N films. A particular attribute of WBN is that its composition for optimum diffusion barriers performance is reached at a low 16 at. % N, which gives it a relatively low resistivity of 220 micro Ohm cm. In this alloy, the constitutive equilibrium compounds are presumable tungsten nitride and baron nitride. We have even synthesized W Re B ($ReW+ReB_2$). This barrier demonstrates clearly that it is fruitless to raise the crystallization temperature off an amorphous metallic film (from 700°C to 900°C by the addition of baron) if its ability to react with the adjacent materials is not suppressed as well.

In all, we can say that the conceptual basis for the understanding of these novel alloys has become fairly solid. Many questions remain open, though. There is an obvious need to characterize this group of novel materials with respect to their physical (electrical, mechanical, and optical) and chemical corrosion properties.

Novel materials bring forth novel application. To identify these require a knowledge of the new properties the material offer. This is why we have initiated various collaborations with groups that are equipped to perform various characterizations of our films. A very successful one has been that with Dr. George F. McLane at the Army Research Laboratory, Ft. Monmouth, NJ. 07703, who has studied several ways to pattern Ta Si N and Ti Si N by various reactive ion etches. Ongoing collaborations address internal friction, hardness, friction and Young's modules. Another has been with William J. Danksher of Motorola's Phoenix Corporate Research Laboratories, in Tempe, AZ 85284. He and his co-workers have developed primary x-ray mask for highest-resolution lithography made of 500 nm thick amorphous Ta SI N films. The two main advantages off this alloy in that application are that (i) the absence of polycrystalline structure allows for a superior sharpness off the live definition upon reactive ion etching, and (ii) the compressive stress that exists in the as - deposited films can be entirely eliminated by thermal annealing. In both respects, Ta SI N outperforms the gold films now used in that application. We helped in getting started with this project at Motorola. The idea for this application came from Dr. Joseph Mogab at Motorola's Advanced Products R & D Laboratory in Austin, TX 78762 where I gave a talk on our work on these films in June 1992.

Although originally developed for Cu metallization of silicon integrated circuit, we established that these same films are also highly effective diffusion barriers for aluminum metallization. Shallow u+p junction diodes maintain their integrity event above the melting point of aluminum where barriers of 130 nm thickness interpassed between the silicon and the aluminum or (Mo,Ta, or W) Si N of optimal compositions. This stability can be partially attributed to a self - sealing Al N layer that grows at the barrier/aluminum interface.

Differences between the various Tm SI N alloys do exist. An important aspect is the strength with which nitrogen is bonded in the alloy. Ta SI N performs best, W Si N worst but still quite acceptably. Polycrystalline Ti N is currently an accepted standard for diffusion barrier applications Ti Si N, being only slightly different in composition from Ti N, has the highest acceptability for the industry. We have therefore undertaken a very complete study of its structure, electrical resistivity and crystallization upon thermal annealing. Ti Si N differ somewhat from the other Tm Si N alloys in its structure, which tends towards nanocrystallinity. A mixed structure off crystalline Ti N and amorphous Si-N is proposed for some nitrogen-rich films. A 100 nm film of Ti_{34} Si_{23} N_{43} prevents copper from reaching a shallow silicon n+p junction below during a 850°C/30 min. annealing in vacuum. A 10 nm film still holds during 650°C/30 min. This result is very significant, because the thickness of a barrier must be scaled down to such low values when the contact vies in an integrated circuit shrink to deep sub-micro sizes. We have also tested.

Two additional successful applications of Tm Si N films worth mentioning are the suppression of Cu diffusion into SiO_2 by only 10 nm of Ta Si N for an $Cu/SiO_2/Si$ capacitor during 300°C annealing for 80h under electric fields in excess of 1MV/cm, and the demonstration of a stable ohmic contact to n-type GaAs by separating the lower Pt/Ge/Au contact with a 90 nm thick Ta Si N barrier from the gold overlayer. Contact resistivities of about $5x10^{-6}$ Ohm cm2 were achieved that safely survived 450°C for 15 min.

Finally, a significant effort was undertaken in the final phase of the grant to clarify the reaction of thin metal films with β-SiC (Re, Pt, Ta, W) and with diamond. Re is thermodynamically stable with SiC at all temperatures and annealing durations considered (<1200°C/1h), Pt forms only silicides and carbides. Contact resistivity measurements were also performed. Revealed that the electrical properties of the contact depends on features and processes that are in the range of 10 nm or less, because even for the thermodynamically stable SiC/Re contact, the contact resistivity decreases 10 - fold to $1x10^{-5}$ Ohmicm upon annealing at 900°C for 30 min. although no reaction can be detected by cross-sectional transmission electron diffraction.